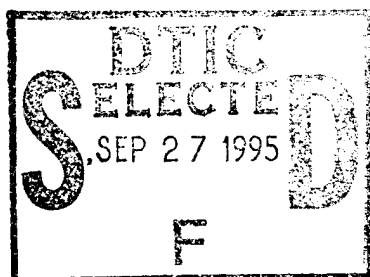# FINAL TECHNICAL REPORT

ON

ELECTRICAL PROPERTIES OF SCHIFF BASE SALTS

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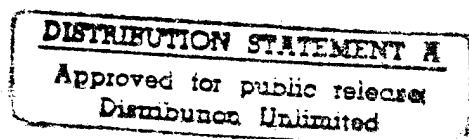
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TABLE OF CONTENTS

ABSTRACT:

An electromagnetic evaluation was made on a series of Schiff Base Salts produced by Hoffmann-LaRoche Inc. The evaluation included standard and nonstandard tests in an attempt to determine time or physical condition dependent phenomena. The results were not successful in detecting a loss capability which would make these salts useful as a passive radar absorber in a coating or other material system.

As a result of this evaluation, the iodine ion was identified as a potential source of electromagnetic loss. This was further investigated in a series of starch iodine compounds. The first set demonstrated an increase in the loss for an iodine concentration of about 6.5%. A second set of starch iodine compounds was produced with iodine concentrations more closely grouped around 6.5%. Tests on this set confirmed a peaking of the loss for iodine concentrations in the range of 6.5% to 7%. The level of the loss factor was such that electromagnetic absorption could be obtained in a material combination containing these iodine compounds. This was not attempted since additional characterization of the starch iodine was required.

ACKNOWLEDGEMENTS:

1.0 INTRODUCTION/MOTIVATION

Some provocative news stories were published attesting to the capabilities of Schiff Base Salts (SBS) as a radar absorber. Boeing was naturally interested and began a search for reliable sources of the Salts. We linked up with Hoffman LaRoche, Inc. which, because of their extensive background in retinal compounds, had the ingredients and ability to produce a range of SBS compounds. We obtained from them a sample of All Trans Retinal (ATR) perchlorate. We put this gray powder into a matrix and produced a 0.2-in thick flat sample of the uniformly mixed combination. After curing, this was taken to a radar backscatter range where the specular reflective characteristics were determined with respect to a flat metal plate in two radar bands — 26-40 GHz and 75-100 GHz. The material performed very much like a pure dielectric at the lower frequency band. However, in the upper frequency band, a null was detected at 94 GHz. This was of interest since there was significant loss there (20 db) and relatively little loss a few GHz away. Subsequent calculations and observation of the backscatter frequency scan showed that this effect was not caused by quarter wave cancellation effects. Possible uses could be made of such a material if the frequency and absorption could be controlled by say varying the concentration of the salts, the thickness of the sample plus mixing the salt with a variety of other lossy materials.

This was the motivation for doing an investigation of a number of Schiff Base Salts compounds to determine whether there were unique electrical absorption characteristics peculiar to these molecular absorbers.

2.0 APPROACH

The result of numerous discussions between Hoffmann LaRoche, ONR and Boeing, was a plan to investigate a series of salts which included three classes: all trans retinal (ATR), etreinate (ETR) and APROCORATINAL (APO). Within each class, salts were discussed and selections made based upon availability and cost of isomers, difficulty in producing the salt, safety considerations and obtaining the largest chemical difference between the salts. In this way it was hoped to obtain trends in the electrical properties that would indicate which direction to go in the production of new salts to further enhance or tailor electrical properties for specific purposes. It was hoped that from these measurements the type of loss mechanism could be determined — whether bulk, molecular or quantization, and that material modifications could then be made with predictable consequences.

The electromagnetic evaluation consisted of measurements to ensure that loss was present followed by calculations to determine the magnitude of the electrical properties. Once the loss mechanism was understood, then more accurate measurements of electrical properties would be made for use in design.

3.0 SCHIFF BASE SALT EVALUATION

The selection and synthesis of the Schiff Based Salts used in the evaluation are very well described in a companion report entitled "An Evaluation of Retinal Schiff Base Salts and Related Compounds As Radar Absorbing Agents" put out by Roche Research Center, Hoffmann-LaRoche Inc. on this same ONR contract. In this report, for the sake of completeness, brief descriptions are given of the salts that were selected for evaluation. The electromagnetic evaluation is described which includes non-standard tests which are described in more detail in the appendices.

3.1 SALT SELECTION AND SYNTHESIS

Polyene Schiff Base Salts are polymers containing a double-bonded carbon-nitrogen structure linking divalent groups in the linear backbone of the molecule's polyene chain. The salts are highly polar, black in color and physically resemble graphite. There are of the order of 600 different salts that are physically possible in this class of polymers.

Starting with the ATR percloride Schiff Base Salt as a baseline, the Salt was conceptually broken down into three distinct parts.
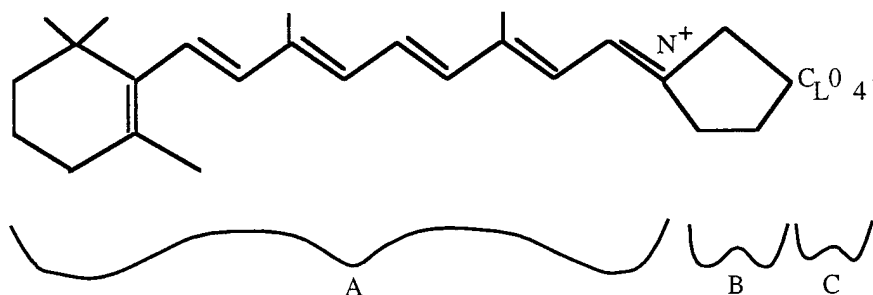
These are the polyene moiety A, the secondary amine B, and the counterion C. Each of these three components was to be varied and new compounds produced for each of the variants. Electromagnetic tests would be performed on these compounds. By comparing the results of these tests, it was hoped that trends would develop as to which constituent had the most effect on the electromagnetic properties. Thus, we could focus on that constituent or constituents and assess related compounds to further define a theory which would relate electromagnetic loss to chemical composition.

Due to difficulties encountered in the synthesis of the secondary amine constituent B, this was not varied in the different compounds produced. Instead, due to the availability of etretinate by Roche, an aromatic moiety was considered.

3.2 AVAILABLE SCHIFF BASE SALTS

Three general classes of salts were produced for evaluation. These can be described as all trans retinal (ATR) Schiff Base Salts, etretinates and β-APO-CAROTENAL. A variety of

Retinal

Etretinate

Apo-Carotenal
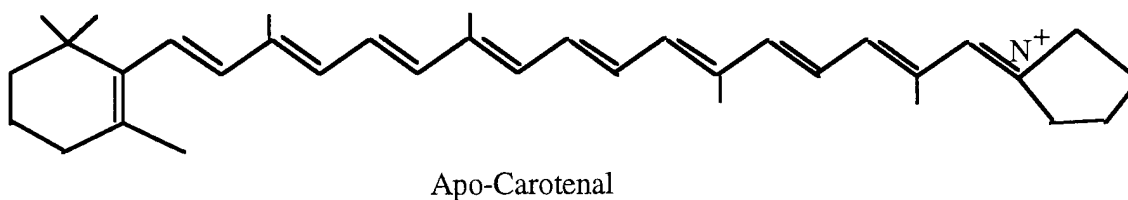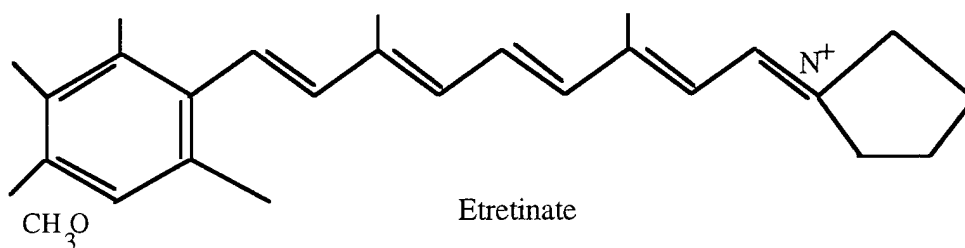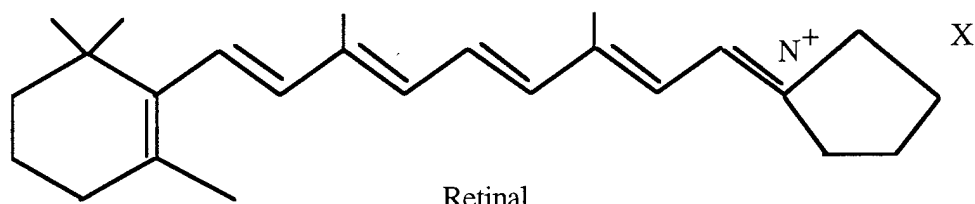
compounds with different counterions were produced for each class. The compounds that were actually tested are listed below.

Class	Counterion
ATR	$CL04 -$
	$C_2 -$
	$BR -$
	$BF_4 -$
	$I -$
	$PF_6 -$
	$I_3 -$
APC	$CL04 -$
ETR	$CL04 -$
	$BF_4 -$

These were supplied to us as powders.

3.3 ELECTROMAGNETIC EVALUATION

The preliminary data showed some loss at 94 GHz. However, if these salts were to be usable as an absorber, some loss would also be required at much lower frequencies. Thus, we began the evaluation at the X-band radar frequency range — 8.2 - 12.4 GHz. The measurement of the original material was made by recording the backscatter while frequency sweeping a 6-inch square of the material embedded in an epoxy binder. The original loss that was detected was seen to be in a fairly narrow frequency range implying that the loss mechanization might be either molecular or quantization. Thus, in all of the measurements that were made, care was taken to watch for sudden and relatively narrow changes in magnitude during the frequency scan.

3.3.1 Powder and Matrix Loaded Sample Measurements

In order to maximize the concentration of the material for the tests, the salts were used in powder form. The powder was placed in waveguide sample holders and gently compressed between two Rexolite supports. The weight and thickness of the material was measured and the electromagnetic properties determined. Two of the salts — the ATR CL- and BR- were extremely hydroscopic. During the time it took to make multiple tests on the salt it was found that the weight increased, the properties changed and the material hardened. At the conclusion of the test, it was necessary to chisel the material out of the sample holder. The limited amount of material available made it impossible to perform any additional tests on these two particular salts.

For all of the remaining salts, 6-inch square samples were made for measurement at higher frequencies. This size has been determined to give accurate results in free-field transmission and reflection tests that are used for determining electrical properties of materials at R and W bands. These samples were made as follows: the amount of salt available was weighed, as was a beaker of CONAP Inc. EN20. EN20 is a clear polyurethane binder which was found to be chemically compatible with all of the available salts.

In order to cast a sample of material in a mold that is 6.25 x 6.25 inches square and of the order of 0.2 inches thick, approximately 30 grams of the mix are required. To assure a uniform and castable mix, the salt is introduced into a little of the binder. Then more of the urethane and more of the salt were added until either all of the salt was used or a saturation point was reach beyond which a uniform crack-free casting could not be made. In this way, a maximum loading of the salt into the binder was achieved, or, all of that particular salt was used up in the process.

A total of eight panels were fabricated with different salts. These were taken to the free space dielectrometer where transmission and backscatter tests were made on the test samples. For the ATR BF-4 samples, no effect of the salt was detectable in the R and W bands compared with a control EN20 panel which was also fabricated and tested. Loss was detected in the ATR I- which was of the same order as the ATR CL_04-. At this time, we did not have the measurement equipment (Hewlett Packard 8510) programmed to automatically calculate the loss factors (ε'') from the reflection and transmission data. For both of these salts, the calculations were not made to get value for the loss factor realizing that it would be of the order of, or less than that of the other

salts tested. For the other salts, no significant electromagnetic loss was detected. A rough average of the loss in each of the bands was taken and the results of the tests are summarized in Figure 1.

3.3.2 Solution Measurements

At this point, the results were somewhat disappointing. It was felt that perhaps the salt was too tightly bound by the EN20 which was preventing any movement of ions along the backbone of the effort to alleviate this, the ATR C_LO4 — which was the most plentiful salt and one of the most lossy, was put into a solution of dimethyl formamide (DMF). It was found to be much more soluble in DMF than in methyl alcohol or Methylene Chloride. In order to obtain electrical properties of the solution, the fluid was placed in fluted core. Five different core samples were tested. One sample was the core by itself, one filled with water as a reference, one with DMF, one with a .01 molar solution of ATR C_LO4^- in DMF and one with a 0.1 solution. This was the maximum amount of salt that we could get into solution without the solids settling out. These panels are shown in Figure 2. Fluted core was used to minimize sag during the measurements. Each of the flutes was filled with the solution and the end sealed with a polyethylene sealant. Standing vertically with the flutes horizontal it was possible to get a uniform thickness of the solution in a flat panel. The properties of the core both along and perpendicular to the flutes were obtained. Similar measurements were made on the core containing the solution and a procedure developed for extracting the electrical properties of the solution. Transmission and reflective measurements were made on the fluids in three radar bands: 2-18 GHz, 26-40 GHz and 75-100 GHz.
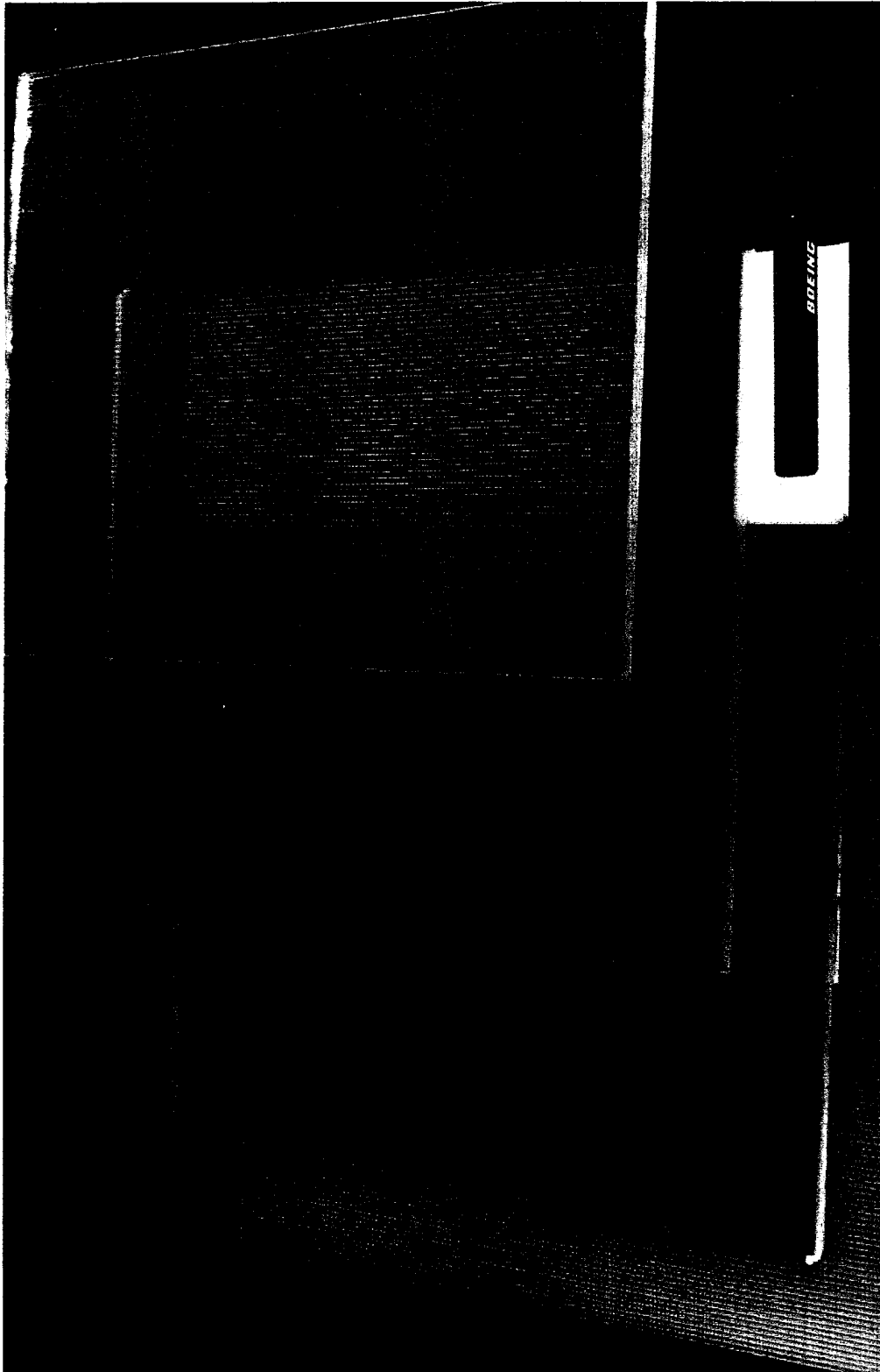
Figure 2. Fluted Core Panels Filled With Solution Of Salt As Well As DMF And Water

Schiff Base Salts

Salt Number	Polyene	Anion	Average Loss Factor		
			Powder	Matrix	
			X Band	R Band	W Band
24-3711/001	ATR	C_LO_4	4	.05	.08
24-3711/002	ATR	C_L	.018	No data	No data
24-3711/003	ATR	B_R	.025	No data	No data
24-3711/004	ATR	BF_4	.04	*	*
24-3711/005	ATR	I	.055	*	*
24-3711/006	ATR	PF_6	.05	.03	.045
24-3711/007	ATR	I^3	.03	.02	.07
24-9353/001	APC	C_LO_4	.023	.008	.09
25-0253/001	ETR	BF_4	.006	.025	.04
25-0253/003	ETR	C_LO_4	.017	.025	.08

* Plots Only - Calculations Not Made

Figure 1. Average Loss Factors of Schiff Base Salts

The conclusions from these tests was that it was not possible to get enough of the salt into solution in order to be able to obtain electrical properties of the salt.

3.3.3 Slurry Measurement

In an attempt to further concentrate the amount of salt and yet allow for any electronic mobility, a large amount of salt was dissolved into methylene chloride. A lightweight but rigid pan was fashioned in a block of Styrofoam as shown in Figure 3. The free-space transmission and reflection was set up to look through the slurry as shown in Figure 4. Scales were set up at the corners of the slurry holder so that the amount of slurry could be tracked as a function of time and correlated with the transmission measurement. The objective of the measurement was to evaporate the solvent and to track the properties of the increasingly concentrated slurry especially
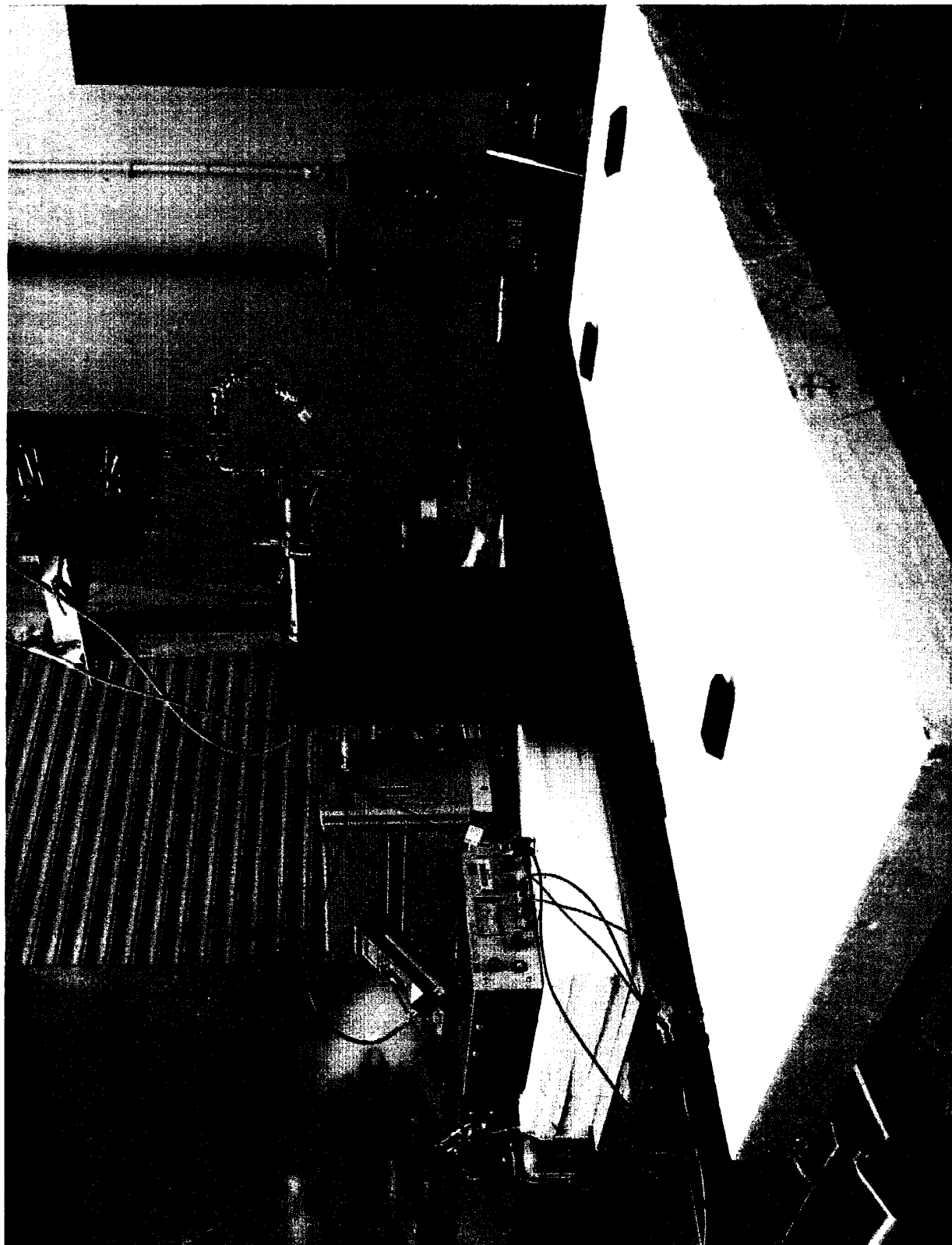
Figure 3. Pan Cut In Foam Block To Hold Highly Concentrated Salt Solution
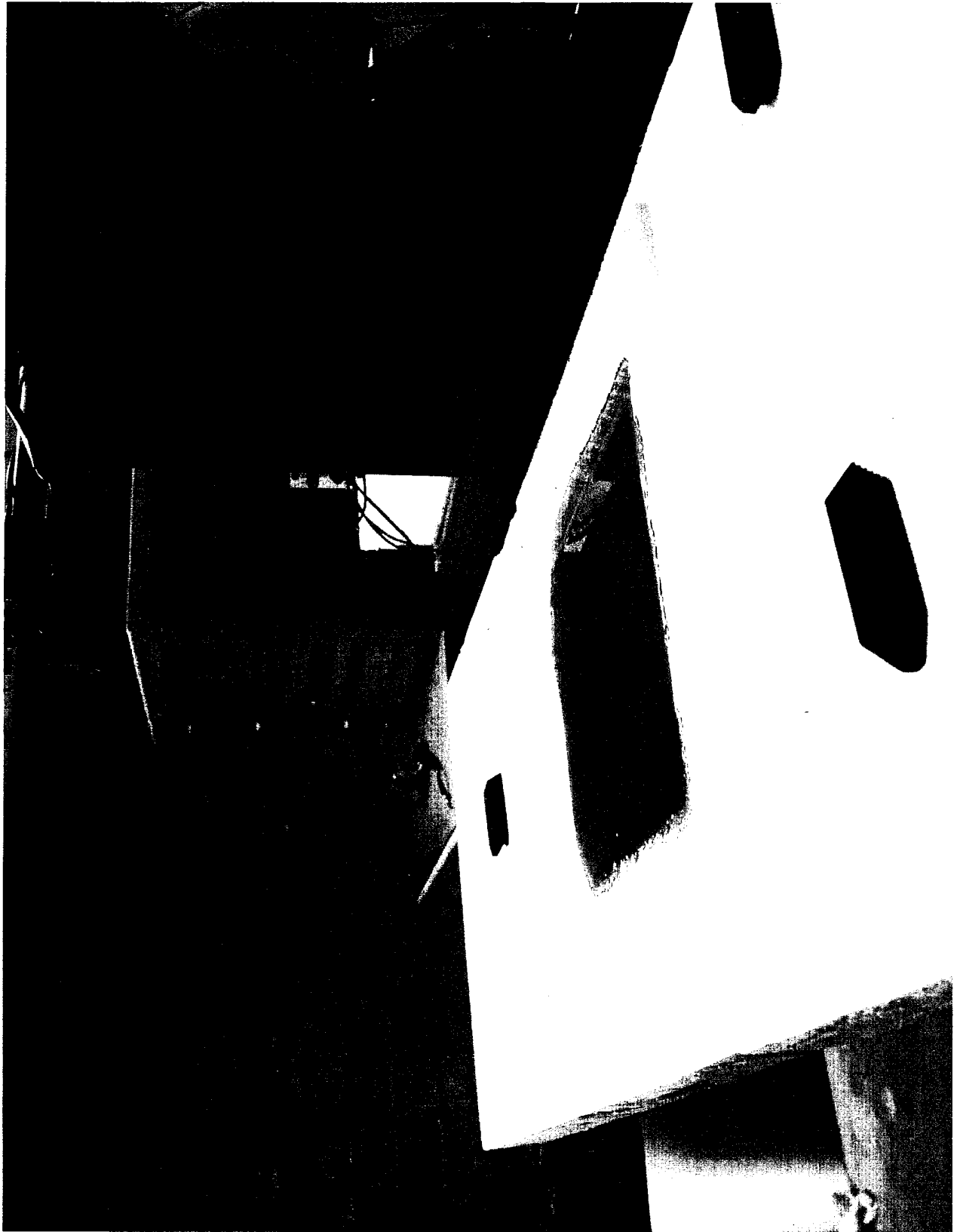
Figure 4. Slurry in Pan. Transmission Horn Positioned Over Slurry.

near the point at which the solvent disappeared to determine whether there is any significant loss in the salts at that point. A description of this test is included in Appendix I. The conclusion from this tests was also that there was no significant electromagnetic loss in the salt.

3.4 CONCLUSIONS OF SCHIFF BASE SALT STUDY

A number of Schiff Base Salts were selected based on availability of constituents, cost and processability. A quantity of each was produced by Hoffmann - LaRoche Inc. and sent to Boeing for electromagnetic evaluation. An attempt was made to obtain the electrical properties of the neat powder and of the powder in a binder by both standard and non-standard methods. Waveguide dielectrometer measurements were made on the powders and free space measurements on the powder loaded matrix samples. In addition, attempts were made to obtain the properties of solutions of the salts and of slurries in which the solvent was being evaporated. In almost all cases electromagnetic loss could be detected but the amount was insignificant compared to what would be required to obtain a "good" electromagnetic absorber. Thus, the conclusion was that; based on the Schiff Base Salts tested, these salts are not a viable constituent of an electromagnetic absorber.

If the goal was merely the advancement, there are some questions that were raised by the study which have not been answered. Some of these are:

1. Can atoms absorb microwave energy and be "pumped" to different energy levels?

2. In a helical structure like the starch iodine be made to vibrate (and absorb energy) only along the axis of the helix.

3. If so, would it then be possible by aligning the starch iodine to "directionalize" the electromagnetic absorption.

4.0 STARCH IODINE COMPOUND INVESTIGATION

4.1 MOTIVATION:

In looking at the results of the Schiff Base Salts Study, of the few anions that showed a modest amount of loss, iodine was selected for further investigation. It has a heavier anion than a perchlorate and is easier to produce. One way to be able to easily vary the iodine loadings is in a

starch. Starch iodine is much cheaper to produce than an iodide Schiff Base Salt. The helical shape of the starch molecule would also allow relatively unrestricted vibration of the iodine ion within the helix if that was the loss causing mechanism.

A series of starch iodine compounds were selected for electromagnetic investigation. These compounds were selected based upon:

- Cost
- Availability of components
- Processability

4.2 INITIAL STARCH IODINE COMPOUNDS:

In order to determine whether concentration of iodine had an effect on electromagnetic loss, five different concentrations of the starch iodine compounds were produced. The iodine concentrations were as follows: 0.48%, 1.56%, 3.26%, 6.49% and 14.44%. The compounds were put into a urethane binder, the sample parameters of which are shown in Figure 5, electrical properties were then determined in a frequency range from 6 to 100 GHz. The results of these tests are shown in Figures 6 through 10. All of the test data is displayed in Figure 11.

Starch Iodine Test Coupons

| Lot No. | Mixture Weight Percentages | | | Sample Thickness |
	Urethane	Starch Iodine	Iodine Loading	
18917-144	29.28	70.72	0.48	.106
18917-122	34.5	65.5	3.26	.115
18917-122	30.7	69.3	3.26	.112
18917-141	31.8	68.2	1.56	.113
18917-142	31.8	68.2	6.49	.118
18917-143	38.6	61.4	14.44	.125

Figure 5. Initial Starch Iodine Test Coupon Parameters

Starch Iodine Compound in Urethane

Frequency Dependance of Loss - 0.48% Iodine
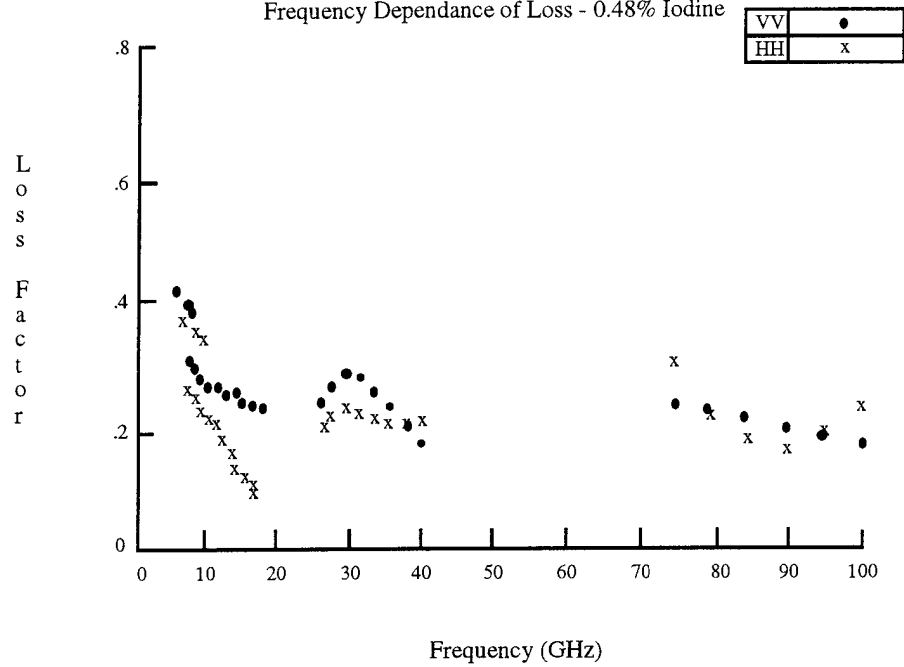
VV	•
HH	x

Figure 6. Loss Factor - 0.4% Iodine

Starch Iodine Compound in Urethane

Frequency Dependance of Loss - 1.56% Iodine
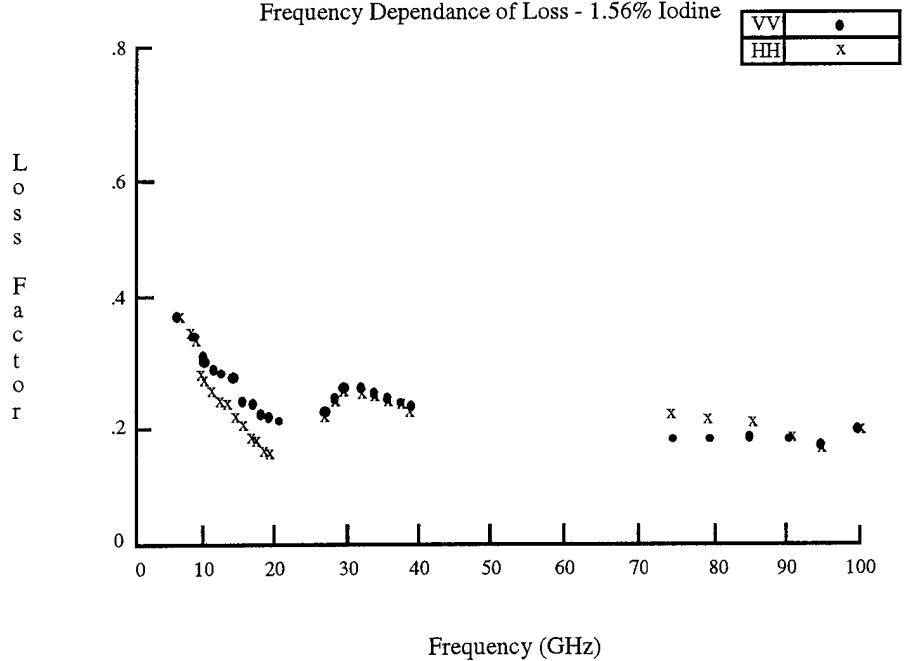
VV	•
HH	x

Figure 7. Loss Factor - 1.56% Iodine

Starch Iodine Compound in Urethane

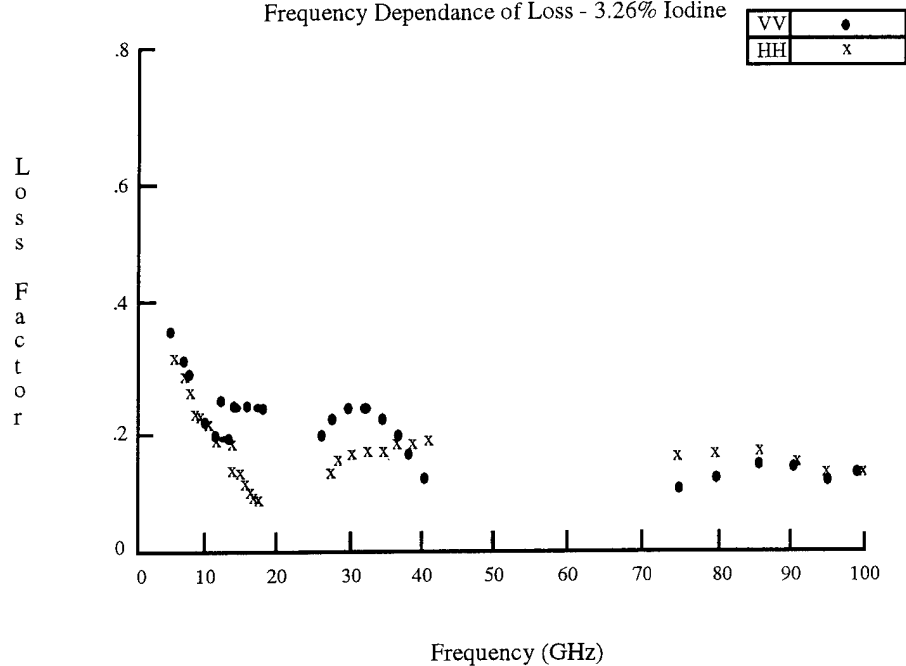Frequency Dependance of Loss - 3.26% Iodine

Figure 8. Loss Factor - 3.26% Iodine

Starch Iodine Compound in Urethane

Frequency Dependance of Loss - 6.49% Iodine
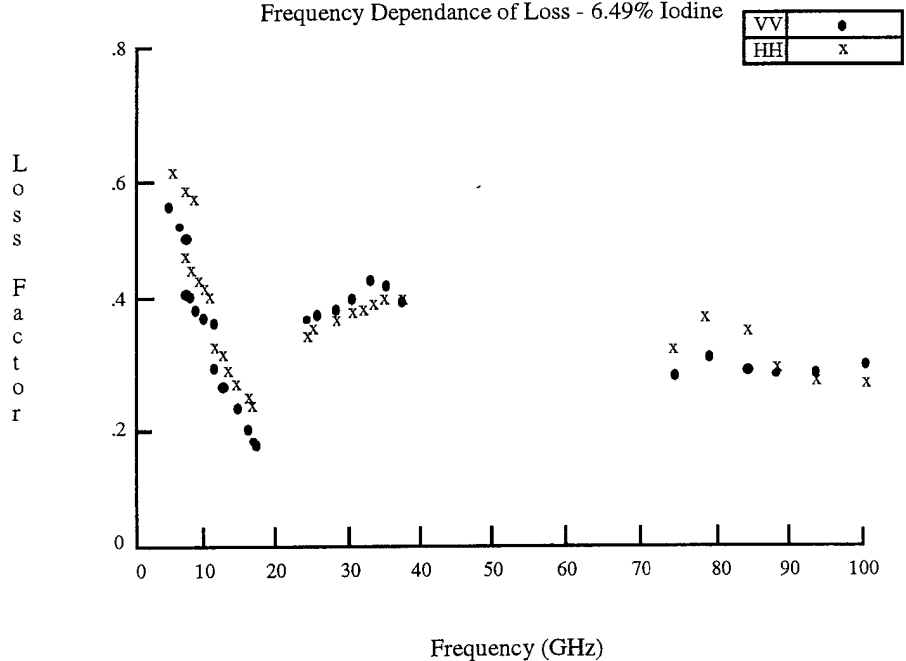
Figure 9. Loss Factor - 6.49% Iodine

Starch Iodine Compound in Urethane

Frequency Dependance of Loss - 14.44% Iodine

VV	●
HH	x

Frequency (GHz)
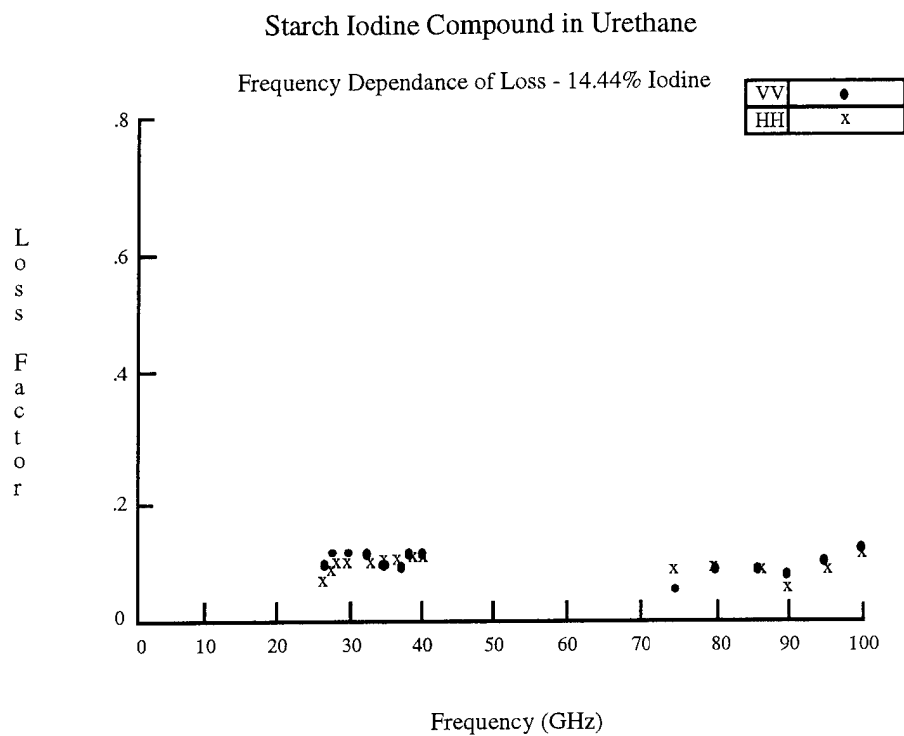
Figure 10. Loss Factor - 14.44% Iodine

Starch Iodine Compound in Urethane

Average Loss for each Starch Loading

0.48%	●
1.56%	x
3.26%	▲
6.49%	■
14.44%	○

Frequency (GHz)

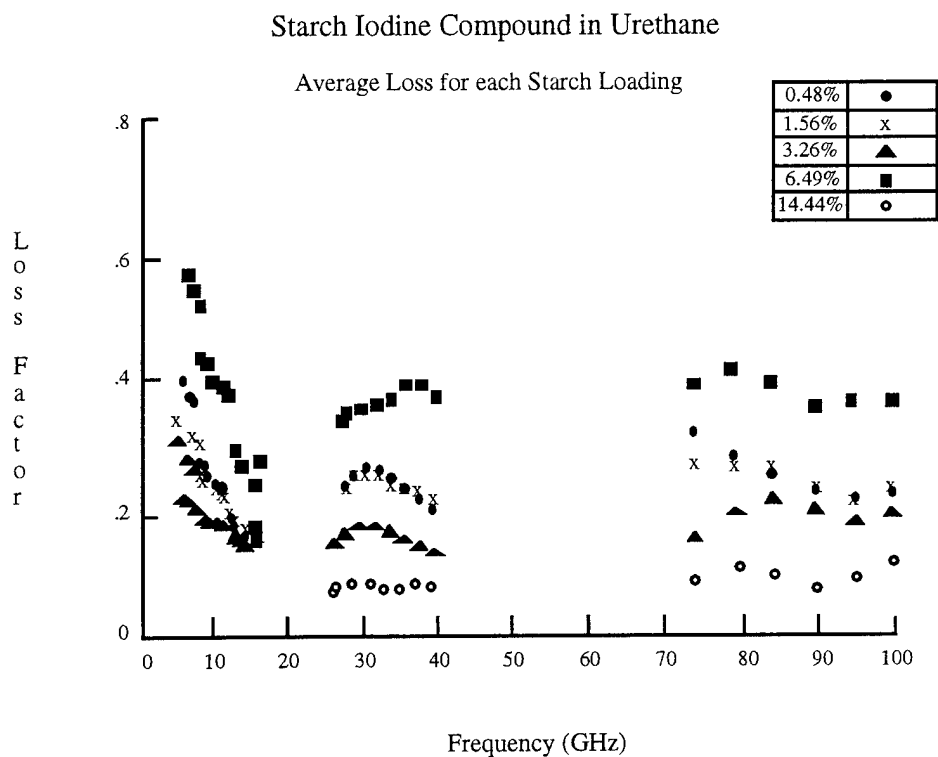*Figure 11. Loss Factors — Initial Starch Iodine Compounds*

Another way of looking at the data was to average all of the data in each band and to plot the average loss within each band against the percent iodine loading. The results are shown in Figure 12.

4.3 SECOND SET OF STARCH IODINE COMPOUNDS

The results of these tests were communicated to Hoffmann-LaRoche. As a result, they produced seven additional salts which were forwarded for electromagnetic evaluation. The iodine concentrations were 4.36%, 5.6%, 6.15%, 6.92%, 7.11%, 8% and 11.66%. These salts were fabricated into samples with parameters as shown in Figure 13. Tests were made on the samples similar to these made on the first set The loss factors were measured on the seven different concentrations in the frequency range 26-40 GHz and 75-100 GHz. The loss was relatively stable with the lowest value for a concentration of 6.92% and the highest loss for a concentration of 7.11%. The lowest level which occurred at 6.92% was surprising in light of the results of the first set of data which showed an increase up to 6.49%.

Some changes occur in the loss for concentrations between 6.5% and 7%. However, the level of loss is still relatively small compared with that available from carbon fiber or carbon powder.

Starch Iodine Compounds - Second Set

Lot No.	Mixture Weight Percentages			Sample Thickness
	EN-20	Starch Iodine	Iodine Loading	
18917-153	38.74	61.25	4.36	.101
18917-154	38.65	61.34	5.60	.101
18917-155	39.09	60.91	6.15	.102
18917-156	38.76	61.03	6.92	.102
18917-157	38.87	61.12	7.11	.101
18917-158	39.03	60.96	8.00	.104
18916-159	36.6	63.39	11.66	.101

Figure 13. Final Starch Iodine Test Coupon Parameters

The dielectric constant also tracks the loss in that when the loss is high, so is the dielectric constant.

4.4 CONCLUSIONS OF STARCH IODINE COMPOUND STUDY

Tests were performed which indicated a peak in the electromagnetic loss for an iodine concentration of about 6.5%. Based on this information, a second set of starch iodine compounds was produced which had a range of iodine concentrations closer to 6.5%. These were also evaluated. Measurements on this second set of samples confirmed the peaking of the loss for an iodine concentration of 6.5% - 7%. Although the loss at the peak was higher than that for a Schiff Base Salt, the level was still not high enough to produce an absorber with properties that would compete against presently used carbon powder, carbon or other filiments or other types of absorbers. Thus, the study was terminated as the materials would not by themselves produce competitive electromagnetic absorbers.

5.0 QUESTIONS FOR FUTURE STUDIES

The conclusions of this program was that the compounds investigated would not result in a high performance radar absorber. However, if the goal was merely the advancement of science, there are some questions that were raised by the study which have not been answered. Some of these are:

1. Can atoms absorb microwave energy and be "pumped" to different energy levels?

2. In a helical structure like the starch iodine, can the atoms be made to vibrate (and absorb energy) only along the axis of the helix.

3. If so, would it then be possible by aligning the starch iodine to "directionalize" the electromagnetic absorption – a polarization sensitive absorber.

APPENDIX I

SLURRY MEASUREMENT

Since we could detect no absorption when the salts were put into solution, we suspected that it might be due to our inability to get a sufficient salt concentration into solution before it began to settle out. In an attempt to get a higher concentration of a uniform solution of the salt, we developed a measurement setup which would allow us to measure the electrical properties as the solution became increasingly concentrated. This setup is shown in Figure A1.

A flat, uniform thickness tray was hollowed out of one flat side of a 4"-thick slab of styrofoam. This tray was lined with visqueen and leveled. The transmission setup was calibrated to negate the effects of the tray. A very high concentration of the salt in methylene chloride was mixed and quickly poured into the tray. The whole measurement apparatus was set up in a paint booth so that the fumes from the evaporating methylene chloride could be harmlessly exhausted. Transmission measurements were taken at intervals as the solution evaporated and the salt concentration increased.

As more of the methylene chloride evaporated, a scum formed on the top of the solution which slowed down the evaporation process quite considerably. This slowed down the interval between measurements such that the 4-hour experiment became a 24-hour one.

The level of concentration of salt was being controlled by accurately weighing the styrofoam tray apparatus, as shown in Figure A1, immediately after the measurement was taken, by balances placed at the corners of the tray. However, the exhaust airflow velocity in the paint booth was not adjustable. It was of such an intensity that the tray would vibrate on the scales. Thus, we were unable to obtain an accurate concentration of salt. Data was taken until evaporation was complete. The results showed a monotonically increasing energy level being recorded as the methylene chloride evaporated. Since we had used up almost all of the salt in the measurement, the experiment could not be repeated.

An analysis of the data showed no significant loss in the salt. The conclusion of the test was that super-saturated solutions did not lead to increased ionic losses in the salt.
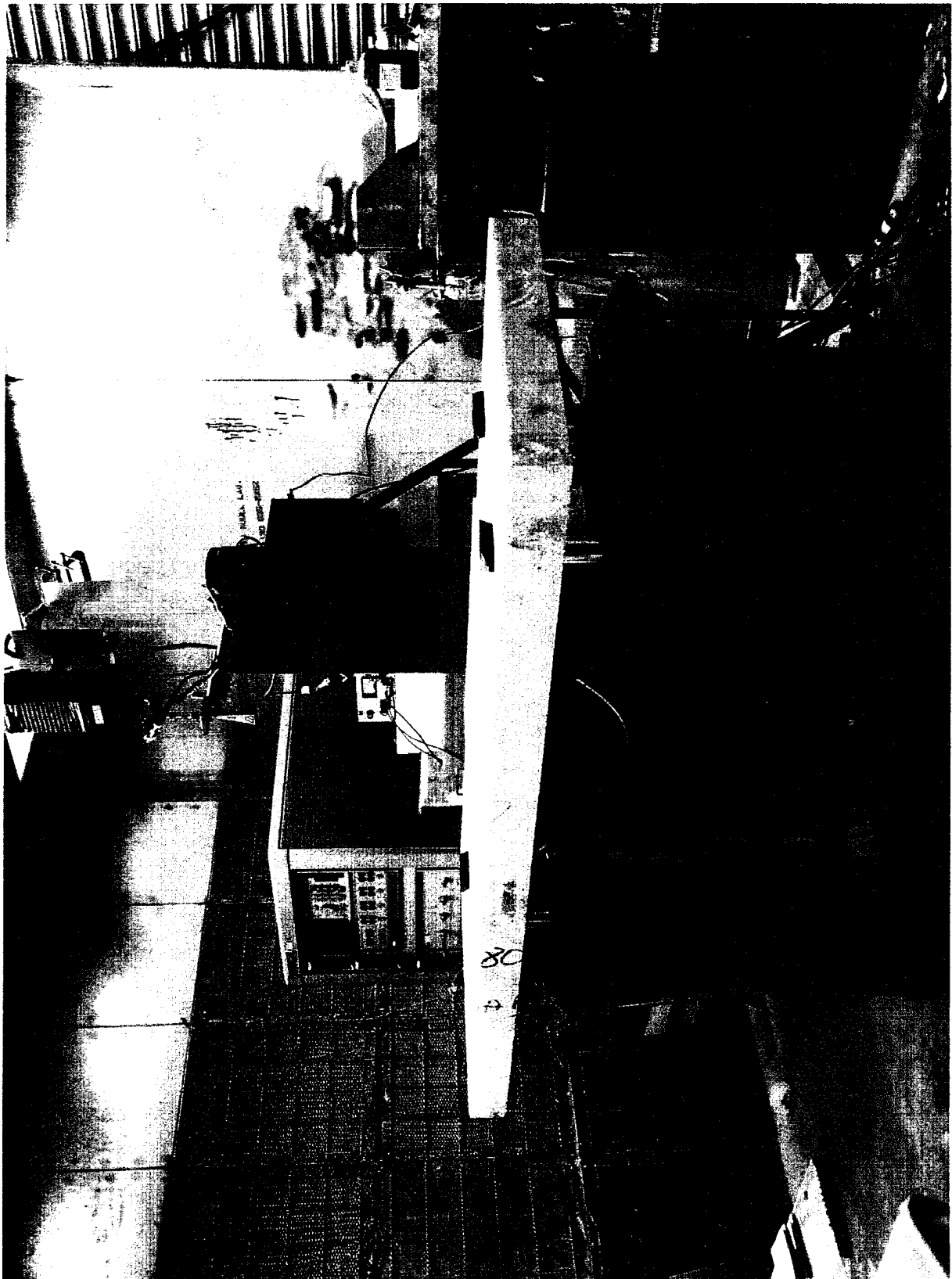
Figure A1. Test Setup Showing Pan, Transmission And Receive Horns And Scales Under Foam Block To Measure Evaporation.